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Term: 6242912

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Search History

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| <u>Set Name</u> side by side | <u>Query</u> | <u>Hit Count</u> | <u>Set Name</u> result set |
|---------------------------------|---|------------------|-------------------------------|
| | <i>DB=USPT,PGPB,JPAB,EPAB,DWPI,TDBD; PLUR=YES; OP=ADJ</i> | | |
| <u>L37</u> | 6242912 | 7 | <u>L37</u> |
| <u>L36</u> | L35 and (weight\$4 or wait\$4) | 2 | <u>L36</u> |
| <u>L35</u> | L34 and (spectr\$4 or amplitude or value or index\$3) | 2 | <u>L35</u> |
| <u>L34</u> | L33 and (water with oil) | 2 | <u>L34</u> |
| <u>L33</u> | L31 and (heavy or crude or hydrocarbon) | 2 | <u>L33</u> |
| <u>L32</u> | ('6005389')[ABPN1,NRPN,PN,TBAN,WKU] | 2 | <u>L32</u> |
| <u>L31</u> | L30 and (cpmg or (spin adj echo) or spin-echo\$2 or spinecho\$2) | 2 | <u>L31</u> |
| <u>L30</u> | L29 and (transverse or "spin-spin" or "spin spin" or "t2" or "t.sub.2" or relax\$8) | 2 | <u>L30</u> |
| <u>L29</u> | L28 and (cutoff or cut-off or "cut off" or threshold\$4) | 2 | <u>L29</u> |

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|------------|---|--------|------------|
| <u>L28</u> | L27 and (oil) | 3 | <u>L28</u> |
| <u>L27</u> | L26 and (water) | 3 | <u>L27</u> |
| <u>L26</u> | L24 and (bitumen) | 4 | <u>L26</u> |
| <u>L25</u> | L24 and (bitrium) | 0 | <u>L25</u> |
| <u>L24</u> | ((324/303)!.CCLS.) | 367 | <u>L24</u> |
| <u>L23</u> | L21 and (temperature or heat\$4) | 6 | <u>L23</u> |
| <u>L22</u> | L21 and (relaxometer or relaxometry) | 1 | <u>L22</u> |
| <u>L21</u> | L20 and (water with oil) | 6 | <u>L21</u> |
| <u>L20</u> | L19 and (water) | 9 | <u>L20</u> |
| <u>L19</u> | L16 and (oil) | 13 | <u>L19</u> |
| <u>L18</u> | L17 and (heavy with (oil or water or fluid)) | 1 | <u>L18</u> |
| <u>L17</u> | L16 and (emuls\$9) | 6 | <u>L17</u> |
| <u>L16</u> | L15 and (oil or water or hydrogeneous or connate or fluid\$5) | 53 | <u>L16</u> |
| <u>L15</u> | L14 and (low\$4 or high\$4 or standard or averag\$4) | 54 | <u>L15</u> |
| <u>L14</u> | L13 and (spectr\$6 or amplitude or value or index\$3) | 54 | <u>L14</u> |
| <u>L13</u> | L12 and (cutoff or cut-off or "cut off" or threshold\$4) | 54 | <u>L13</u> |
| <u>L12</u> | L11 and (weight\$4 or heavy) | 168 | <u>L12</u> |
| <u>L11</u> | L10 and (transverse or "spin-spin" or "spin spin" or "t2" or "t.sub.2" or relax\$8) | 342 | <u>L11</u> |
| <u>L10</u> | L1 and ((low with field) with ((magnetic adj resonance) or MRI or NMR)) | 754 | <u>L10</u> |
| <u>L9</u> | L8 and (low\$4 or high or standard) | 3 | <u>L9</u> |
| <u>L8</u> | L7 and (spectr\$4 or amplitude or value or index\$3) | 3 | <u>L8</u> |
| <u>L7</u> | L6 and (emuls\$9) | 3 | <u>L7</u> |
| <u>L6</u> | L5 and (transverse or longitudinal or "spin-lattice" or "spin-spin" or "spin spin" or "spin lattice" or "t2" or "t.sub.2" or "t.sub.1" or "t1" or relax\$8) | 16 | <u>L6</u> |
| <u>L5</u> | L4 and (weight\$4 or heavy) | 16 | <u>L5</u> |
| <u>L4</u> | L3 and (cutoff or cut-off or "cut off" or threshold\$4) | 19 | <u>L4</u> |
| <u>L3</u> | L2 and (oil or water or hydrogeneous or connate or fluid\$5) | 65 | <u>L3</u> |
| <u>L2</u> | L1 and (relaxometer or relaxometry) | 82 | <u>L2</u> |
| <u>L1</u> | ((magnetic adj resonance) or MRI or NMR) | 145650 | <u>L1</u> |

END OF SEARCH HISTORY



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L26: Entry 1 of 4

File: USPT

Nov 5, 2002

DOCUMENT-IDENTIFIER: US 6477516 B1

TITLE: System and method for predicting parameter of hydrocarbon with spectroscopy and neural networks

Brief Summary Text (4):

Some examples of useful heavy products having properties that must be known or measured are heavy distillation cuts, such as vacuum gasoil, vacuum residua, asphalts, pitches and the like. Asphalts are classified, based on rheological properties that have a temperature dependency, according to the Strategic Highway Research Program (SHRP) parameters which frequently must be determined by performing conventional, time consuming laboratory analysis including aging, further processing and the like. For alternative analytical methods, only one publication (Michon, L.; Hanquet, B.; Diawara, B.; Martin, D.; Planche, J-P. Asphalt Study by Neuronal networks. Correlation between Chemical and Rheological Properties. Energy & Fuel, 11, 1188-93, 1997) has been found which attempts to correlate bitumen rheological properties and average molecular parameters using ^{13}C NMR and neural networks. The quality of the results of Michon et al. does not comply with the precision and low cost needed for a viable commercial application.

Current US Cross Reference Classification (1):

324/303

Other Reference Publication (2):

Estimation of average structural parameters of bitumens by ^{13}C nuclear resonance spectroscopy, Laurent Michon; Didier Martin; Jean-Pascal Planche and Bernard Hanquet; Fuel (1997) vol. 76, No. 1.*

Other Reference Publication (4):

Estimation of Average Structural Parameters of Bitumens ^{13}C Nuclear Magnetic Resonance Spectroscopy, by Michon et al., Fuel, vol. 76, No. 1, pp. 9-15, 1997.



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L26: Entry 2 of 4

File: USPT

Jul 3, 2001

DOCUMENT-IDENTIFIER: US 6255818 B1

TITLE: Method and apparatus for performing magnetic resonance measurements

Brief Summary Text (15):

where HI is the hydrogen index of the formation fluid, and K is a calibration factor that accounts for several tool and external parameters. Relaxation times are related to permeability of the formation as well as the fluid properties and may be used to identify hydrocarbon types. Water relaxation times increase with increasing pore size. Thus, short T1 or T2 times indicate bound water, while long T1 and T2 times are associated with free fluid. For hydrocarbons in water wet rocks, the T1 and T2 times are determined by viscosity. The T1 time increases with decreasing viscosity over the entire hydrocarbon range from bitumen to methane gas. The T2 time follows a similar trend for heavy and medium oils. For lighter hydrocarbons, diffusion effects reduce the T2 time. The effect is most significant for gas. Because of the wide range of pore sizes found in rock formations and the chemical complexity of typical oils, broad distributions of T1 and T2 times are usually observed. Whereas T2 distributions may be estimated by analysis of multi-exponential decays of CPMG echo amplitudes, it is necessary to perform several separate measurements using different polarization times $t_{sub.p}$, in order to properly characterize T1 distributions.

Current US Original Classification (1):

324/303



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L26: Entry 3 of 4

File: USPT

Oct 31, 2000

DOCUMENT-IDENTIFIER: US 6140817 A

TITLE: Magnetic resonance well logging method and apparatus

Detailed Description Text (14):

Despite recent improvements in measuring porosity components with very short $T_{2\rho}$, magnetic resonance measurements can still underestimate bound fluid volume. For example, it has been observed that some mature, dewatered shales have relaxation time components below 0.3 msec. Bitumen volumes are also considerably underestimated by MR measurements. Then $\phi_{D\rho} > BFV$, even when there is no free fluid. Under these circumstances, Equation (9) will erroneously indicate the presence of substantial permeability.

Detailed Description Text (16):

The flag is zero in tight zones and in typical shales. In these zones, no correction to the computed permeability is required. In most other formations; $\phi_{D\rho} - BFV \approx FFI$, so the Flag is near unity, which is denoted "low"; no correction to the computed permeability is required. In dewatered shales and bitumen, $\phi_{D\rho} - BFV > 0$ and $FFI \approx 0$, so the Flag is high. In these zones the permeability can be automatically set equal to an arbitrarily low value. A flow diagram for this processing is described in conjunction with FIG. 9 below.

Current US Original Classification (1):

324/303

End of Result Set



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L26: Entry 4 of 4

File: USPT

Dec 21, 1999

DOCUMENT-IDENTIFIER: US 6005389 A

TITLE: Pulse sequences and interpretation techniques for NMR measurements

Current US Original Classification (1):

324/303

CLAIMS:

20. The method of claim 17 further comprising the step of identifying a portion of the T.sub.2 spectrum as corresponding to very heavy crude hydrocarbons, such as bitumen.

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☐ 1. Document ID: US 6477516 B1

L26: Entry 1 of 4

File: USPT

Nov 5, 2002

US-PAT-NO: 6477516

DOCUMENT-IDENTIFIER: US 6477516 B1

TITLE: System and method for predicting parameter of hydrocarbon with spectroscopy and neural networks

DATE-ISSUED: November 5, 2002

INVENTOR-INFORMATION:

| NAME | CITY | STATE | ZIP CODE | COUNTRY |
|-------------------------|-------------|-------|----------|---------|
| Colaiocco; Silvia Rosa | Miranda | | | VE |
| Espidel; Youssef Euclio | La Victoria | | | VE |

US-CL-CURRENT: 706/21; 324/303

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| Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC |
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☐ 2. Document ID: US 6255818 B1

L26: Entry 2 of 4

File: USPT

Jul 3, 2001

US-PAT-NO: 6255818

DOCUMENT-IDENTIFIER: US 6255818 B1

TITLE: Method and apparatus for performing magnetic resonance measurements

DATE-ISSUED: July 3, 2001

INVENTOR-INFORMATION:

| NAME | CITY | STATE | ZIP CODE | COUNTRY |
|-----------------------|------------|-------|----------|---------|
| Heaton; Nicholas J. | Houston | TX | | |
| Davies; Dylan H. | Sugar Land | TX | | |
| Taherian; M. Reza | Stafford | TX | | |
| Sun; Boqin Q. | Sugar Land | TX | | |
| Sezginer; Abdurrahman | Houston | TX | | |

US-CL-CURRENT: 324/303; 324/318

| | | | | | | | | | | |
|-----------|-------|----------|-------|--------|----------------|------|-----------|-----------|-------------|------|
| Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC |
| Draw Desc | Image | | | | | | | | | |

☐ 3. Document ID: US 6140817 A

L26: Entry 3 of 4

File: USPT

Oct 31, 2000

US-PAT-NO: 6140817

DOCUMENT-IDENTIFIER: US 6140817 A

TITLE: Magnetic resonance well logging method and apparatus

DATE-ISSUED: October 31, 2000

INVENTOR-INFORMATION:

| NAME | CITY | STATE | ZIP CODE | COUNTRY |
|----------------------|------------|-------|----------|---------|
| Flaum; Charles | Ridgefield | CT | | |
| Kleinberg; Robert L. | Ridgefield | CT | | |

US-CL-CURRENT: 324/303; 324/300

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| Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC |
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☐ 4. Document ID: US 6005389 A

L26: Entry 4 of 4

File: USPT

Dec 21, 1999

US-PAT-NO: 6005389

DOCUMENT-IDENTIFIER: US 6005389 A

TITLE: Pulse sequences and interpretation techniques for NMR measurements

DATE-ISSUED: December 21, 1999

INVENTOR-INFORMATION:

| NAME | CITY | STATE | ZIP CODE | COUNTRY |
|---------------------|-------------|-------|----------|---------|
| Prammer; Manfred G. | Downingtown | PA | | |

US-CL-CURRENT: 324/303; 324/300

| | | | | | | | | | | |
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| Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC |
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|--|-----------|
| BITUMEN.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 19202 |
| BITUMAN.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 15 |
| BITUMENS.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 1686 |
| BITUMANS | 0 |
| (24 AND BITUMEN).USPT,PGPB,JPAB,EPAB,DWPI,TDBD. | 4 |
| (L24 AND (BITUMEN)).USPT,PGPB,JPAB,EPAB,DWPI,TDBD. | 4 |

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[Previous Page](#)

[Next Page](#)

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Search Results - Record(s) 1 through 3 of 3 returned.

☐ 1. Document ID: US 6255818 B1

L28: Entry 1 of 3

File: USPT

Jul 3, 2001

US-PAT-NO: 6255818

DOCUMENT-IDENTIFIER: US 6255818 B1

TITLE: Method and apparatus for performing magnetic resonance measurements

DATE-ISSUED: July 3, 2001

INVENTOR-INFORMATION:

| NAME | CITY | STATE | ZIP CODE | COUNTRY |
|-----------------------|------------|-------|----------|---------|
| Heaton; Nicholas J. | Houston | TX | | |
| Davies; Dylan H. | Sugar Land | TX | | |
| Taherian; M. Reza | Stafford | TX | | |
| Sun; Boqin Q. | Sugar Land | TX | | |
| Sezginer; Abdurrahman | Houston | TX | | |

US-CL-CURRENT: 324/303; 324/318

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|---------------------------|-----------------------|--------------------------|-----------------------|------------------------|--------------------------------|----------------------|---------------------------|---------------------------|-----------------------------|----------------------|
| Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KIMC |
| Draw Desc | Image | | | | | | | | | |

☐ 2. Document ID: US 6140817 A

L28: Entry 2 of 3

File: USPT

Oct 31, 2000

US-PAT-NO: 6140817

DOCUMENT-IDENTIFIER: US 6140817 A

TITLE: Magnetic resonance well logging method and apparatus

DATE-ISSUED: October 31, 2000

INVENTOR-INFORMATION:

| NAME | CITY | STATE | ZIP CODE | COUNTRY |
|----------------------|------------|-------|----------|---------|
| Flaum; Charles | Ridgefield | CT | | |
| Kleinberg; Robert L. | Ridgefield | CT | | |

US-CL-CURRENT: 324/303; 324/300

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|---------------------------|-----------------------|--------------------------|-----------------------|------------------------|--------------------------------|----------------------|---------------------------|---------------------------|-----------------------------|----------------------|
| Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KIMC |
| Draw Desc | Image | | | | | | | | | |

☐ 3. Document ID: US 6005389 A

L28: Entry 3 of 3

File: USPT

Dec 21, 1999

US-PAT-NO: 6005389

DOCUMENT-IDENTIFIER: US 6005389 A

TITLE: Pulse sequences and interpretation techniques for NMR measurements

DATE-ISSUED: December 21, 1999

INVENTOR-INFORMATION:

| NAME | CITY | STATE | ZIP CODE | COUNTRY |
|---------------------|-------------|-------|----------|---------|
| Prammer; Manfred G. | Downingtown | PA | | |

US-CL-CURRENT: 324/303; 324/300

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| Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KMC |
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| Term | Documents |
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| OIL.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 1043861 |
| OILS.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 201490 |
| (27 AND OIL).USPT,PGPB,JPAB,EPAB,DWPI,TDBD. | 3 |
| (L27 AND (OIL)).USPT,PGPB,JPAB,EPAB,DWPI,TDBD. | 3 |

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[Previous Page](#)

[Next Page](#)

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Search Results - Record(s) 1 through 2 of 2 returned.

☐ 1. Document ID: US 6140817 A

L31: Entry 1 of 2

File: USPT

Oct 31, 2000

US-PAT-NO: 6140817

DOCUMENT-IDENTIFIER: US 6140817 A

TITLE: Magnetic resonance well logging method and apparatus

DATE-ISSUED: October 31, 2000

INVENTOR-INFORMATION:

| NAME | CITY | STATE | ZIP CODE | COUNTRY |
|----------------------|------------|-------|----------|---------|
| Flaum; Charles | Ridgefield | CT | | |
| Kleinberg; Robert L. | Ridgefield | CT | | |

US-CL-CURRENT: 324/303; 324/300

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| Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | Claims | KWIC |
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☐ 2. Document ID: US 6005389 A

L31: Entry 2 of 2

File: USPT

Dec 21, 1999

US-PAT-NO: 6005389

DOCUMENT-IDENTIFIER: US 6005389 A

TITLE: Pulse sequences and interpretation techniques for NMR measurements

DATE-ISSUED: December 21, 1999

INVENTOR-INFORMATION:

| NAME | CITY | STATE | ZIP CODE | COUNTRY |
|---------------------|-------------|-------|----------|---------|
| Prammer; Manfred G. | Downingtown | PA | | |

US-CL-CURRENT: 324/303; 324/300

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|------------|-------|----------|-------|--------|----------------|------|-----------|-----------|-------------|--------|------|
| Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | Claims | KWIC |
| Drawn Desc | Image | | | | | | | | | | |

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|---|-----------|
| CPMG.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 297 |
| CPMGS.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 9 |
| SPIN.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 148343 |
| SPINS.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 15212 |
| ECHO.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 45410 |
| ECHOES.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 13486 |
| ECHOS.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 2228 |
| ECHOE.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 44 |
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| SPIN-ECHO.DWPI,TDBD,EPAB,JPAB,USPT,PGPB. | 1136 |
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[Previous Page](#)

[Next Page](#)

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☐ 1. Document ID: US 6140817 A

L36: Entry 1 of 2

File: USPT

Oct 31, 2000

US-PAT-NO: 6140817

DOCUMENT-IDENTIFIER: US 6140817 A

TITLE: Magnetic resonance well logging method and apparatus

DATE-ISSUED: October 31, 2000

INVENTOR-INFORMATION:

| NAME | CITY | STATE | ZIP CODE | COUNTRY |
|----------------------|------------|-------|----------|---------|
| Flaum; Charles | Ridgefield | CT | | |
| Kleinberg; Robert L. | Ridgefield | CT | | |

US-CL-CURRENT: 324/303; 324/300

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|-----------|-------|----------|-------|--------|----------------|------|-----------|-----------|-------------|------|
| Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC |
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☐ 2. Document ID: US 6005389 A

L36: Entry 2 of 2

File: USPT

Dec 21, 1999

US-PAT-NO: 6005389

DOCUMENT-IDENTIFIER: US 6005389 A

TITLE: Pulse sequences and interpretation techniques for NMR measurements

DATE-ISSUED: December 21, 1999

INVENTOR-INFORMATION:

| NAME | CITY | STATE | ZIP CODE | COUNTRY |
|---------------------|-------------|-------|----------|---------|
| Prammer; Manfred G. | Downingtown | PA | | |

US-CL-CURRENT: 324/303; 324/300

| | | | | | | | | | | |
|-----------|-------|----------|-------|--------|----------------|------|-----------|-----------|-------------|------|
| Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC |
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| Term | Documents |
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[Previous Page](#)

[Next Page](#)

End of Result Set



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L36: Entry 2 of 2

File: USPT

Dec 21, 1999

DOCUMENT-IDENTIFIER: US 6005389 A

TITLE: Pulse sequences and interpretation techniques for NMR measurements

Abstract Text (1):

An NMR pulse sequence and signal processing method is disclosed for measurement of fast decay response signals from materials containing a fluid state. The proposed pulse sequence and processing method are applicable in borehole NMR logging as well as measurements of attributes of man-made or natural materials. The disclosed pulse sequence comprises a series of short NMR pulse trains separated by intervals which are shorter than the time required for polarization of nuclear magnetization in bulk fluids of the fluid state. By stacking response signals to increase the signal to noise ratio, time domain data is obtained that generally corresponds to transverse decay components as short as about 0.5 ms. Various attributes of the materials being investigated can be derived in a single measurement.

Brief Summary Text (5):

Another approach frequently used during open-hole logging is to perform bulk conductivity measurements in order to identify and separate oil-bearing zones which have low conductivity, from water-bearing zones which have high conductivity. However, in practice the interpretation of measurement data is typically obscured by the presence of highly-conductive clay attached to or interspersed with sand grains. Due to the fact that no simple measurement exists for generating quantitative in situ estimates of the amount of clay and the water volume bound to the clay, the interpretation of in situ conductivity data is still more of an art than a science.

Brief Summary Text (6):

The amount and type of clay in a formation is interesting to reservoir and to production engineers in its own right. For example, swelling and/or dislodging of certain clay particles may clog an otherwise permeable sand. Conventional logging tools have been often characterized in terms of their response to clay minerals and/or clay-bound water. In fact, most conventional logging measurements (such as neutron-absorption cross section, bulk density, natural gamma-ray radiation, spontaneous electric potential, sonic wave transit time, photoelectric absorption factor, etc.) respond in a qualitative way to the presence of clay in the formation being investigated, mostly because clays tend to accumulate heavy minerals. More information is contained in D. V. Ellis, "Well Logging For Earth Scientists," Elsevier 1987, chapter 19: "Clay Typing and Quantification from Logs," which chapter is incorporated herein by reference. Still, no single reliable method exists currently for estimating the parameters of the clay present in a formation. FIG. 1 shows the standard rock porosity model which provides an illustration of the issues discussed above. In particular, as shown in FIG. 1, the total porosity space is occupied by water and hydrocarbons. The volume excluded from what is designated in the figure as "effective porosity" is the clay-bound water fraction.

Brief Summary Text (7):

It is well known that the signal measured by NMR logging tools is proportional to the mean density of hydrogen nuclei in the fluid that occupies the pore space. Pulsed NMR measurements performed downhole are sensitive to the amount of hydrogen atoms from liquid or gaseous materials, but not from solid-state rock. Therefore, in principle, NMR is a truly lithology-independent porosity measurement. However, with reference to FIG. 1, current logging tools register only part of the total porosity of the formation because hydrogen nuclei in the rock matrix and those associated with clay particles relax too rapidly to be detected and measured under the limited signal-to-noise (SNR) conditions available downhole.

Brief Summary Text (8):

Accordingly, it is clear that the difference between a "total porosity" measurement (derived, for example, from a bulk density measurement, neutron absorption and/or sonic transit time) and the NMR-measured porosity can be interpreted as the amount of clay-bound water. See for example the disclosure in U.S. Pat. No. 5,557,200 assigned to the assignee of the present application, which is hereby incorporated by reference for all purposes. However, prior art methods require the use of separate techniques to measure the total porosity of a formation. In fact, obtaining an accurate estimate of this total porosity is still relatively difficult. Furthermore, an NMR measurement itself can be depressed by fluid effects, such as deficient hydrogen index, long polarization times T1, etc.

Brief Summary Text (13):

2. Miller, M. N. et al.: "Spin Echo Magnetic Resonance Logging: Porosity and Free Fluid Index Determination," paper SPE 20561 presented at the 1990 SPE Annual Technical Conference and Exhibition, Proceedings, 321.

Brief Summary Text (17):

6. Korringa, J., Seevers, D. O. and Torrey, H. C.: "Theory of Spin Pumping and Relaxation in Systems With a Low Concentration of Electron Spin Resonance Centers," Phys. Rev. 127 (1962) 1143.

Brief Summary Text (18):

7. Fripiat, J et al.: "Thermodynamic and Microdynamic Behavior of Water in Clay Suspensions and Gels," J. Colloid. Interface Sci. 89 (1982) 378.

Brief Summary Text (19):

8. Woessner, D. E.: "An NMR Investigation Into The Range of the Surface Effect on the Rotation of Water Molecules," J. Magn. Reson. 39 (1980) 297.

Brief Summary Text (26):

The present invention defines a novel pulse sequence, logging technique and a signal processing scheme that employ existing NMR instruments or logging tools to directly quantify the amount of bound water in the materials under investigation, or clay-bound water in the formation. The method of the present invention is characterized by the rapid accumulation of only those NMR signal components which are typical for clay-bound water and have very fast T1 and/or T2 relaxation times. The signal-to-noise ratio can typically be enhanced by a factor of seven or more, compared to the standard NMR measurement.

Brief Summary Text (28):

Finally, in accordance with the present invention one can improve the resistivity interpretation model based on the use of parallel conduction paths for clay-bound water and non-clay-bound water. Specifically, having obtained each fluid volume from the NMR measurement separately simplifies the log interpretation and provides more accurate estimates of all parameters of interest. Additional properties of materials under investigation can be obtained by combining the measurements in accordance with the present invention with external measurements, as known in the art.

Drawing Description Text (3):

FIG. 2 illustrates a phase-cycled CPMG pulse sequence used with conventional NMR logging tools.

Drawing Description Text (14):

FIG. 11 illustrates an example of T_{sub.2} spectrum obtained from signals in a laminated sand/shale earth formation.

Drawing Description Text (17):

FIG. 14 illustrates the behavior of very fast relaxation components measured in various lithologies in accordance with the method of the present invention.

Detailed Description Text (2):

There are two versions of modern pulse-NMR logging tools in use today: the centralized MRIL.RTM. tool made by NUMAR Corporation, and the side-wall CMR tool made by Schlumberger. The MRIL.RTM. tool is described, for example, in U.S. Pat. No. 4,710,713 to Taicher et al. and in various other publications including: "Spin Echo Magnetic Resonance Logging: Porosity and Free Fluid Index Determination," by Miller, Paltiel, Millen, Granot and Bouton, SPE 20561, 65th Annual Technical Conference of

the SPE, New Orleans, La., Sept. 23-26, 1990; "Improved Log Quality With a Dual-Frequency Pulsed NMR Tool," by Chandler, Drack, Miller and Prammer, SPE 28365, 69th Annual Technical Conference of the SPE, New Orleans, La., Sept. 25-28, 1994). Details of the structure and the use of the MRIL.RTM. tool are also discussed in U.S. Pat. Nos. 4,717,876; 4,717,877; 4,717,878; 5,212,447; 5,280,243, 5,309,098, and 5,412,312, all of which are commonly owned by the assignee of the present invention.

Detailed Description Text (5):

With reference to the attached drawings, FIG. 2 shows a standard pulse sequence typically employed by NMR logging tools, such as the Numar MRIL.RTM. and the Schlumberger CMR tools. As shown in FIG. 2, a wait time interval ($T_{sub.w}$) of approximately 0.5-10 sec is used first to allow for polarization of the formation by the tool's static magnetic field. Then, a Carr-Purcell-Meiboom-Gill (CPMG) pulse-echo train is executed, consisting of an excitation pulse (A) and an alternating sequence of refocusing pulses (B). Following each pair of excitation pulse and a refocusing pulse, acquisition window (C) is applied next. Complex data from such a pair of echo trains are co-added on an echo-by-echo basis to remove certain artifacts and to enhance the NMR signal, as known in the art. More pairs may be added to enhance the signal-to-noise ratio. The echo train, consisting of a superposition of exponentially decaying signals is then submitted to a processing scheme which calculates the underlying decay modes of the received NMR echo signal.

Detailed Description Text (6):

Specifically, a processing method (Prammer's method) for calculating the underlying decay modes of the NMR signal is described in U.S. Pat. No. 5,517,115 to the present inventor. The content of this patent is hereby expressly incorporated by reference for all purposes. As discussed in the patent, if such a measurement is repeated many times while the tool is held stationary, it is possible to identify the portion of the clay-bound water in the signal.

Detailed Description Text (7):

NMR RESPONSE OF CLAY-BOUND WATER

Detailed Description Text (8):

As discussed above with reference to the rock porosity model in FIG. 1, conventional hydrogen-NMR responds well to hydrogen in fluids and very poorly or not at all to hydrogen in solids. Thus, downhole NMR logging is only concerned with the fluid-filled porosity of the rock space. The rate of signal decay is a strong function of the local surface-to-volume ratio in the pore space. Both $T_{sub.1}$ (longitudinal) and $T_{sub.2}$ (transversal) relaxation times, which are on the order of a few seconds in fresh water, can be reduced by several orders of magnitude once the liquid is introduced into the pore space and is in contact with the grain surfaces. The effect has been explained in physical terms by the theory of surface relaxation. The first generation of NMR logging tools was limited to an intrinsic "dead time" of 20 ms, corresponding to a $T_{sub.2}$ cutoff time of about 30 ms, which in many shaly sand formations separates irreducible from movable fluids. Today's commercial pulsed-NMR tools also quantify the capillary-bound ("irreducible") regime in the $T_{sub.2}$ range of 4-30 ms.

Detailed Description Text (9):

Clay-bound water, however, has much faster $T_{sub.2}$ times due to the enormous specific surface area of clays (up to 800 m^{sup.2} /g). Details on specific surface areas and NMR measurements on smectites and kaolinites can be found in Fripiat et al. D. E. Woessner has studied longitudinal relaxation times ($T_{sub.1}$) at 8 and 25 MHz in aqueous solutions of hectorite. He found a perfectly linear relationship between the relaxation rate ($1/T_{sub.1}$) and the amount of dry clay per water volume. The plausible explanation for these data is the combination of two factors: (1) a short-range dipole-dipole surface relaxation effect that does not extend more than 1-2 layers of water molecules from the solid surface, and (2) fast exchange between this mono-molecular surface water layer and the clay-associated water volume due to thermal diffusion.

Detailed Description Text (10):

In order to more closely resemble the downhole measurement, laboratory NMR experiments were performed at 1 MHz to determine transverse relaxation times $T_{sub.2}$. Representative samples of montmorillonite (a smectite), illite, kaolinite and chlorite were obtained from the Source Clay Minerals Repository of the Clay Mineral Society, located at the University of Missouri. Table 3 summarizes the

sample clay types and their properties. The samples were prepared by adding 0%, 12.5%, 25% and 50% by weight of synthetic sea-water brine, mixing the paste and pressing the mixture at 2500 psi. NMR amplitudes and T_{sub.2} distributions of the sealed samples were measured in a commercially available core analyzer, operating at 1 MHz, a temperature of 25.degree. C., and at echo spacings (T_{sub.e}) of 0.3 ms and 0.5 ms. The water content was determined by weighing each sample before and after overnight vacuum-drying at 103.degree. C. The results are listed in Table 4.

Detailed Description Text (11):

Except for the montmorillonite sample SWy-2, no clay sample had an NMR signal without having water added to it. SWy-2 absorbs 7% water by weight under normal indoor humidity conditions. At this concentration, the bound water relaxes extremely fast with poor visibility at the 0.5 ms echo spacing. As more brine is added, T_{sub.2} increases up to 1 ms, while all absorbed water becomes NMR-visible. The latter fact is consistent with the "fast exchange" hypothesis borne out of Woessner's data. The clay-bound water in the other clay samples is always fully visible at T_{sub.e} = 0.5 ms. As expected, T_{sub.2} increases linearly with the amount of water absorbed. The illite sample could not absorb more than 15.8% brine, the kaolinite was limited to 20.0% and the chlorite to 7.5%. Selected T_{sub.1} measurements were performed, yielding ratios of T_{sub.1}/T_{sub.2} between 1.5 and 2 as indicated in Table 4.

Detailed Description Text (12):

The "fast exchange" hypothesis predicts a linear relationship between relaxation rate and the surface-to-volume ratio: ##EQU1##

Detailed Description Text (13):

The laboratory measurements allow one to estimate values for the surface relaxivity $\rho_{sub.2}$ from specific surface areas (Table 3) and from the water-to-dry ratios (Table 4). As shown in Table 4, the computed values are almost constant (0.8-1 $\mu\text{m/s}$), except for the chlorite sample, which is probably compromised by an overestimated specific surface area. Apparently, clay mineralogy has little influence on the T_{sub.2} values, but rather the surface-to-volume ratio is the dominant factor. Furthermore, these values for surface relaxivity are substantially smaller than those reported in the literature for sandstones (of the order of 5-20 $\mu\text{m/s}$). Fortunately for a downhole measurement, the low surface relaxivities of clays imply a range of T_{sub.2} values that can be measured with the current MRIL logging tool technology.

Detailed Description Text (14):

The cation exchange capacity (CEC, Table 3) of clays is fundamental to the conversion of bulk resistivity measurements into water saturation and hence hydrocarbon saturation estimates. The number of available exchange sites is proportional to a clay's specific surface ratio, and therefore the observed T_{sub.2} can be turned into an indicator of CEC: T_{sub.2} components greater than 3 ms indicate little or no CEC; the range 1-2 ms is associated with illite-type CEC's, and T_{sub.2} 's less than 1 ms indicate smectites with high CEC values.

Detailed Description Text (15):

A field study was conducted at Shell's Stribling #1 test well near Johnson City, Tex., to confirm the laboratory T_{sub.2} data and to prove the concept of a downhole clay-bound water measurement. The well was drilled and cored in 1964 and is open-hole from casing at 305 ft to total depth at 1268 ft. Its geological composition is well characterized, consisting of shaly sands and shales below 1100 ft. The heavy and variable clay contents made this well very suitable for the present study. Illite as the dominant clay mineral in these formations.

Detailed Description Text (16):

An MRIL engineering test tool was used to acquire station logs in the various shaly sandstone sections. FIGS. 2 and 3 show representative data collected at a station opposite a formation with about 50% bioturbated shale. Carr-Purcell-Meiboom-Gill echo trains with 1000 data points and an echo-to-echo spacing of 0.51 ms were acquired and averaged for 15 minutes in order to increase the signal-to-noise ratio, i.e. the precision of the measurement. The very fast initial decay visible in FIG. 2 has a time constant of 1 ms and is due to clay-bound water.

Detailed Description Text (18):

FIG. 4 illustrates the result of applying Prammer's processing method to the data shown in FIG. 3. Each peak in this "relaxation spectrum" shown in FIG. 4 corresponds

to a major relaxation mode of the underlying signal. In particular, from left to right one can identify three peaks: (a) clay-bound water, (b) capillary bound water and (c) movable water. In accordance with the Prammer's processing method the integrated areas under the peaks are proportional to the individual water volumes. In the example illustrated in FIG. 4, the amount of clay-bound water volume is 4.8%; capillary-bound water volume is 4.9%; and movable water volume is 1.8% of the total volume.

Detailed Description Text (19):

FIG. 4 also illustrates the customary T₂ "cutoff" values which, in this example are 3 ms for the clay vs. non-clay boundary and 30 ms for non-movable vs. movable water. While these cutoff values are not universally applicable, they are fairly standard in the logging industry for use in oil reservoirs in shaly sandstone foundations.

Detailed Description Text (20):

In the stationary example illustrated in FIG. 4 it took about 15 minutes to accumulate the stationary data. In a moving tool, of course, much less time is available for accumulation. Therefore, given that the achievable signal-to-noise ratio is limited by basic physical parameters and the tool construction, less information can be extracted from the log data. In particular, T_{sub.2} information below 3 ms becomes very unreliable and "regularization" schemes must be applied to suppress very fast relaxation modes in the data.

Detailed Description Text (22):

The novel pulse sequence in accordance with a preferred embodiment of the present invention is shown in FIG. 5. The first part of the sequence is identical to the one shown in FIG. 2. As shown in FIG. 5, immediately following the regular CPMG train is issued a series of short echo trains characterized by short wait intervals (T_{sub.s}). Preferably, about 0.5-10 seconds are required for the long wait period T_{sub.w}, followed by a standard CPMG pulse-echo train of several 100 ms duration, followed by a short wait time T_{sub.s} having about 10-100 ms duration. The short wait time T_{sub.s} is followed next by a CPMG train having about 1-100 echoes, which is followed by another short wait time, and so forth. In a specific example, 16 echoes can be used. Typically, for every long pulse train, between about 10 to 100 short echo trains are used. The sequence of short pulse trains is phase-cycled, i.e., alternate trains use phase-reversed refocusing pulses. All echoes from the short trains are co-added to yield several final short recovery data points. In a specific example using 16 echoes, corresponding number of short recovery data points are generated.

Detailed Description Text (24):

Track 2 in FIG. 6 illustrates the first three echoes resulting from co-adding 50 short-recovery measurements in place of a single standard measurement. The echo-to-echo spacing in this experiment was 0.51 ms. The signal-to-noise ratio for the short-recovery measurements was improved by a factor of $\sqrt{50}$ over the standard log. Notably, the echo amplitudes in track 2 are depressed compared with those in track 1, because they are associated with fast T_{sub.1} recovery. Tracks 3 and 4 present two more logging passes over the same depth interval, and are equivalent to tracks 1 and 2, respectively.

Detailed Description Text (26):

(A) The standard CPMG data obtained in block 10 is subjected in block 20 to the T_{sub.2} inversion procedure outlined in U.S. Pat. No. 5,517,115, using a pre-specified model of principal T_{sub.2} relaxation components. For example, the numerical sequence: 4, 8, 16, 32, 64, 128, 256, 512, 1024, 2048 ms can be used in a specific embodiment. Block 50 in FIG. 7 indicates the T_{sub.2} relaxation spectrum obtained on output of block 20. The sum of all detected modes obtained in block 60 is designated as the effective, or standard NMR porosity. The T_{sub.2} relaxation spectrum in block 50 is used to differentiate capillary-bound water from movable fluids (water or hydrocarbons).

Detailed Description Text (27):

(B) The accumulated fast-T_{sub.s} short echo trains in block 30 are subjected in block 40 to T_{sub.2} inversion using another pre-specified set of relaxation components. In the specific embodiment illustrated in FIG. 7, the sequence: 0.5, 1, 2, 4, 8, 2048 ms, of relaxation components was used. In this example, amplitudes found to relax with 4, 8 or 2048 ms are discarded as being incompletely polarized. On the other hand, the amplitudes associated with 0.5, 1 and 2 ms relaxation times represent the fast relaxation spectrum (block 50) and are next summed in block 70 to

yield what is (tentatively) equated to "clay-bound porosity."

Detailed Description Text (28):

As shown in FIG. 7, a complete $T_{sub.2}$ distribution can be assembled in block 50 from concatenated responses in blocks 20 and 40. In the specific example shown, the $T_{sub.2}$ comprises the 0.5, 1, 2, 4, 8, 16, 32, 64, 128, 256, 512, 1024 and 2048 ms relaxation modes. The sum of all these responses is taken in block 80 as a measure of the total formation porosity. In accepting this measure it is assumed that the rock is completely filled with liquids of hydrogen indices equal to the one of water. Tables 1 and 2 provide a complete listing of the stationary and logging measurement parameters, respectively.

Detailed Description Text (29):

The processing scheme described above with reference to FIG. 7 is an illustration of a preferred embodiment of the present invention, in which the porosity measurements are obtained on the basis of the $T_{sub.2}$ relaxation spectrum approach. In an alternative embodiment of the present invention, equivalent processing can be done in the time domain. Briefly stated, in this alternative embodiment the "standard" NMR echo data is used to obtain a rough estimate of the time dependency of the early data points. Next, the high-signal-to-noise, high-quality data points from short echo trains are used to refine this estimate and to draw an accurate relaxation curve, interpolated back to time zero. The resulting composite relaxation curve can then be submitted to $T_{sub.2}$ inversion to produce a unified $T_{sub.2}$ distribution.

Detailed Description Text (32):

There exist many models for interpreting resistivity measurements in shaly sand formations. Most of these methods incorporate a model of parallel conduction paths for electrical current flowing through water with conductivity $C_{sub.w}$ and through clay-bound water with conductivity C_{cw} . The $C_{sub.w}$ parameter can be deduced from log responses in 100%-water-filled formations or can be measured on produced water samples. Parameter C_{cw} is frequently modeled is a simple function of temperature using, for example, the formula

Detailed Description Text (34):

Further inputs required in the measurement interpretations are the water saturation associated with $C_{sub.w}$ ($S_{sub.w}$) and the water saturation associated with $C_{sub.cw}$ ($S_{sub.wb}$). See, for example the discussion in U.S. Pat. No. 5,557,200 assigned to the assignee of the present application, the content of which is expressly incorporated by reference for all purposes. Both parameters $S_{sub.w}$ and $S_{sub.wb}$ can be obtained from NMR measurements using the novel pulse sequence and the signal processing method of the present invention.

Detailed Description Text (35):

In particular, as indicated above, the area under the $T_{sub.2}$ distribution gives the total volume available for fluid accumulation. The "fast" end of the $T_{sub.2}$ distribution is mostly associated with clay-bound water; the partial "fast $T_{sub.2}$ " area divided by the total area yields the parameter S_{wb} . Similarly, the water saturation $S_{sub.w}$ can be extracted from the "slow $T_{sub.2}$ " area of a $T_{sub.2}$ distribution. The proposed method of interpretation represents a significant improvement over the published prior art, in which saturation parameters had to be estimated from separate and often inaccurate measurements.

Detailed Description Text (38):

(1) FIG. 8A illustrates a regular set of echoes from a CPMG sequence with a wait time $T_{sub.w}$ such that

Detailed Description Text (40):

(2) FIG. 8B illustrates a set of echoes, which is heavily overlapped to give a very high signal-to-noise ratio, obtained by stacking short echo trains with a wait time $T_{sub.PR}$ such that

Detailed Description Text (45):

where $A(T_{sub.2})$ is a $T_{sub.2}$ distribution, and N is a normal noise distribution with zero mean and a standard deviation $\sigma_{sub.R}$. The initial amplitude (time=0) corresponds to full polarization.

Detailed Description Text (46):

The stacked echo set illustrated in FIG. 8B can be expressed mathematically as $\sum A(T_{sub.2})$ where $A(T_{sub.2})$ is the same $T_{sub.2}$ distribution, $T_{sub.PR}$ is the partial

recovery time, $T_{sub.1}$ ($T_{sub.2}$) is the $T_{sub.1}$ distribution associated with the $T_{sub.2}$ distribution, and NA is the number of averages used to obtain the data stack. Due to the short repeat time, the initial amplitude does not correspond to full magnetization.

Detailed Description Text (49):

The difference D between amplitudes is expressed as

Detailed Description Text (54):

A composite $T_{sub.2}$ distribution can be calculated from the composite train S.sub.C by means of the inversion method disclosed in U.S. Pat. No. 5,517,115 to Prammer.

Detailed Description Text (56):

Consider an earth formation consisting of laminations of shale and sand, as shown in FIG. 10. Note that the thickness of an individual sand or shale layer may range from approximately 1 mm to many meters and may not always be resolved by the aperture (range of integration) of the NMR instrument. As shown in the art, hydrocarbon fluids can only migrate to and accumulate in the sand layers. In the following description, the following definitions are used:

Detailed Description Text (62):

However, using the method of the present invention, the N/G ratio can be estimated directly as follows. A typical $T_{sub.2}$ spectrum is shown in FIG. 11. For many clay minerals (illites, smectites), water occupying the shale porosity relaxes with NMR relaxation times less than about 3 ms. Therefore, the part of the $T_{sub.2}$ spectrum below approximately 3 ms can be identified as shale porosity .o slashed. sub.shale ; the rest is identified as sand porosity .o slashed. sub.sand. The capacity of a reservoir to hold hydrocarbons is proportional to the sand portion of the total porosity. Equation 9A above can be rewritten as: ##EQU6##

Detailed Description Text (64):

Reference is made to "Measurements of Clay-Bound Water and Total Porosity by Magnetic Resonance Logging" by Prammer et al., The Log Analyst, November/December 1996 pp. 61-69. As shown in this paper, an earth formation can consist of the following components:

Detailed Description Text (67):

3) water bound to clay minerals,

Detailed Description Text (71):

By estimating .o slashed. sub.shale from the $T_{sub.2}$ spectrum, as discussed above, and by noting the dominant $T_{sub.2}$ relaxation time of the clay-bound water, an estimate of the clay mineral component type can be obtained from Table 4.

Detailed Description Text (72):

Furthermore, having identified the clay type, by assuring an average water weight-to-dry clay weight ratio, an estimate of the dry clay weight can be obtained. Again, refer to Table 4, columns 2 and 5.

Detailed Description Text (74):

In highly laminated reservoirs, as illustrated in a diagram form in FIG. 10, the clay mineral type is fairly uniform. In this case, the relative water content and the average pore size in the shale is dominated by the pressure compacting a shale lamination. The more pressure, the smaller the pore sizes become, resulting in a decrease in $T_{sub.2}$. By following the trend in shale $T_{sub.2}$'s vertically, a pressure profile can be obtained, indicative of high or low pressure differentials.

Detailed Description Text (78):

The second log example (FIG. 13) illustrates the advantages of the lithology-independence of .PHI..sub.MRT, obtained in accordance with the present invention. In a water-filled or oil-filled formation of unknown lithology, the matrix density can be estimated as follows: Using the total MRIL porosity (in decimal units; .PHI..sub.MRT is shown in track 3 as bold line) as the porosity term in the bulk density response,

Detailed Description Text (79):

and setting .rho..sub.fl =1.0 g/cm.sup.3 for water, an apparent matrix density .rho..sub.app can be computed: ##EQU7## The result of this calculation is shown in FIG. 13. At X623 ft, an abrupt change in lithology exists from an apparent matrix

density of .about.2.68 g/cm.sup.3 to .about.2.85 g/cm.sup.3. From core analysis, it is known that the sandstone above X623 consists mostly of quartz (2.657 g/cm.sup.3) and that the limestone/dolomite mix below X623 is mostly dolomite (2.85 g/cm.sup.3). Track 3 shows density porosities for .rho.=2.65 g/cm.sup.3 (dashed line), and for .rho.=2.85 g/cm.sup.3 (solid line), to be in excellent agreement with the MRIL porosity .PHI..sub.MRT (bold solid line). In mixed or unknown and gas-free formations, the NMR measurement can provide a stand-alone porosity answer that is independent of core analysis, and/or crossplot techniques that rely on different tool responses.

Detailed Description Text (80):

FIG. 14 illustrates the behavior of the very fast relaxation components computed in accordance with the present invention in various lithologies. Track 1 is the spectral gamma ray in API units 1-150, and track 3 contains porosities on a scale of 0 to 0.3. Density porosity calibrated for a sandstone matrix (.rho.=2.65 g/cm.sup.3) is shown dashed; effective MRIL porosity is light solid; total MRIL porosity is shown in bold solid. Evidently, the density log is affected by hole rugosity in several places, whereas the MRIL is not (for example, at X295, X322, X334, X402, X431 and X52). In track 2, the difference .PHI..sub.MRT -.PHI..sub.MRE is broken down into the fastest three T_{sub.2} relaxation components. The individual bands in track 2 indicate the individual intensities of the relaxation modes: 2 ms (left, black), 1 ms (center, white) and 0.5 ms (right, black). The sandstone sections (X340-X390 and X418-X595) show good agreement between the density log and .PHI..sub.MRT. In the very clean section from X555 to X595, no clay-bound signal is detected (track 2), and full agreement exists between density porosity, .PHI..sub.MRE and .PHI..sub.MRT. In the shaly sections (high gamma ray readings) a characteristic clay-bound water signal develops with a T_{sub.2} of 1-2 ms. Density porosity and .PHI..sub.MRT continue to agree, while effective porosity is considerably reduced and at places vanishes. Differences between density porosity and total MRIL porosity, where MRIL porosity is higher than density porosity; are indicative of lithologies with matrix densities greater than 2.65 g/cm.sup.3. This is the case in the top shale (above X281), where recomputing the density response yields an apparent matrix density close to 2.80 g/cm.sup.3. The clay-bound signal has a clear signature of 1-2 ms. Below the shale section, in the interval X281-X330, layers of limestone and shale are interspersed. For example, the limestone at X310 is identified by high effective porosity and an undercall in sandstone density porosity. The 1-2 ms T_{sub.2} signature is missing in this section, replaced by a very fast decay below 1 ms, which could be due to microporosity in the limestone or due to interbedded, dense shale thinner than the logging tools' resolution limits.

Detailed Description Text (83):

As shown in the U.S. Pat. No. 5,672,968, concrete which is used for construction can be analyzed to determine its structural properties, such as strength, potential for shrinkage and others in the final cured concrete. As the concrete is a mixture of various materials and includes a water portion, the method of the present invention can be used to determine various attributes of the materials, such as the curing properties of the various cement mixtures.

Detailed Description Text (93):

T_{sub.1} magnetic resonance longitudinal relaxation time

Detailed Description Text (94):

T_{sub.2} magnetic resonance transversal relaxation time

Detailed Description Text (97):

T_{sub.w} wait time

Detailed Description Paragraph Equation (4):

$S_{sub.R}(t) = \int_0^t A(T_{sub.2}) \cdot e^{-t/T_{sub.2}} d(T_{sub.2}) + N(0, \sigma_{sub.R})$ (2)

Detailed Description Paragraph Table (4):

TABLE 4

RESULTS OF LABORATORY T_{sub.2} MEASUREMENTS T_{sub.2} of clay- Apparent .rho..sub.2
Water Weight NMR Visibility bound water at surface per dry clay at Te = 0.5 ms Te -
0.5 ms relaxivity Clay ID weight (%) (ms) (ms) (.mu.m/s) Remarks

| | | | | | | | | | | | | | | | SWy-2 7.0 | |
|----|-------|-----|-----------------------------------|------|-----|------|-----|------|-----|--------|------|------|-----|-----|-----------|--------------------------------|
| 20 | -- | -- | <u>T_{sub.2}</u> < 0.2 ms | 18.9 | 90 | 0.3 | 1 | 31.1 | 100 | 0.5 | 1 | 54.4 | 100 | 1 | 0.9 | <u>T_{sub.1}</u> = 1.5 |
| ms | 1Mt-1 | 8.8 | 90 | 1 | 0.9 | 15.8 | 100 | 2 | 0.8 | KGa-1b | 11.7 | 100 | 8 | 0.8 | 17.4 | 100 |
| | | | | | | | | | | | | | | | 12 | 0.8 |
| | | | | | | | | | | | | | | | 20.0 | 100 |

16 0.7 T.sub.1 = 30 ms C.Ca-2 7.5 100 5 0.4 .rho..sub.2 may be too low due to over estimated surface area

Measurements were made at 1 MHz and at 25.degree. C. on the clay samples listed in Table 1. Samples were saturated with different amounts of brine pressed at 2500 psi and sealed. Water weight was determined from weight loss by overnight drying in a vacuum chamber at 103.degree. C. NMR visibility is the ratio of calibrated NMR amplitude (in ml of water) per ml of water content determined from weight loss. Apparent transversal surface relaxivities .rho..sub.2 were calculated from specific surface areas # (Table 1), the waterto-dry weight ratios and from T.sub.2 's.

Current US Original Classification (1):
324/303

Other Reference Publication (1):

Morriss et al., "Hydrocarbon Saturation and Viscosity Estimation from NMR Logging in the Belridge Diatomite," 35th SPWLA Annual Logging Symposium (Jun. 19-22, 1994), pp. 1-24.

Other Reference Publication (3):

Schlumberger Wireline & Testing, "Combinable Magnetic Resonance tool reliably indicates water-free production and reveals hard-to-find pay zones," (Jun. 1995).

Other Reference Publication (9):

Miller et al., "Spin Echo Magnetic Resonance Logging: Porosity and Free Fluid Index Determination," Society of Petroleum Engineers (1990), pp. 321-334.

Other Reference Publication (15):

Straley et al., "NMR in Partially Saturated Rocks: Laboratory Insights on Free Fluid Index and Comparison with Borehole Logs," SPWLA Annual Logging Symposium (Jun. 27, 1991) pp. 40-56.

Other Reference Publication (17):

Clavier et al., "The Theoretical and Experimental Bases for the `Dual Water` Model for the Interpretation of Shaly Sands," Journal of Petroleum Technology (Apr. 1984), pp. 3-15.

Other Reference Publication (18):

Waxman et al., "Electrical Conductivities in Oil-Bearing Shaly Sands," Society of Petroleum Engineers Journal (1968) pp. 107-122.

CLAIMS:

1. A nuclear magnetic resonance (NMR) method for measuring an indication of attributes of materials containing a fluid state, the method comprising the steps of:

(a) applying in a pre-determined sequence at least two short NMR pulse trains, each pulse train comprising at least one pulse and resulting in at least one response signal from said materials, the interval T.sub.s between any two short pulse trains being less than the time required for polarization of substantially all nuclear magnetization in bulk fluids of the fluid state contained in said materials;

(b) stacking NMR response signals from said at least two short NMR pulse trains to obtain time domain data indicative of fast decay components of the fluid state contained in said materials;

(c) combining said at least two short NMR pulse trains with one or more regular NMR pulse-echo trains, wherein a regular NMR pulse train is preceded by a recovery time T.sub.w sufficient to substantially polarize all nuclear magnetization in the fluid state and the duration of each of said one or more regular NMR pulse trains is longer than the duration of each of said short NMR pulse trains; and

(d) determining overall relaxation properties of the fluid state contained in said materials from the combination of said at least two short NMR pulse trains with said one or more regular NMR pulse-echo trains.

3. The method of claim 2 wherein said at least two short NMR pulse trains are Carr-Purcell-Meiboom-Gill (CPMG) pulse-echo trains.

5. The method of claim 1 further comprising the steps of converting the time domain data into T.sub.2 spectrum data; and

determining attributes of said materials from the T.sub.2 spectrum data.

6. The method of claim 1 further comprising the step of converting time domain data obtained from (i) said stacked short NMR pulse trains and (ii) from said regular pulse-echo trains into combined T.sub.2 spectrum data; and

extracting information about attributes of said materials from said combined T.sub.2 spectrum data.

7. The method of claim 6 wherein said attributes of said materials comprises the total magnetic resonance porosity .PHI..sub.MRT of said materials which is computed as:

$$.PHI..sub.MRT = .PHI..sub.MRE + .PHI..sub.B$$

where:

.PHI..sub.MRE is the magnetic resonance effective porosity derived from components in the combined T.sub.2 spectrum that correspond to said regular pulse NMR trains, and

.PHI..sub.B is the bound porosity derived from components in the combined T.sub.2 spectrum that correspond to said stacked short NMR pulse trains.

11. The method of claim 1 further comprising the step of deriving a measure of shale volume from the T.sub.2 spectrum data.

13. The method of claim 1 wherein said at least two short NMR pulse trains are applied to depth of investigation in the borehole which is shallow compared with the depth of investigation in the borehole for said regular CPMG pulse-echo measurements of said earth formation.

14. The method of claim 13 further comprising the steps of converting time domain data obtained from (i) said stacked short NMR pulse trains and (ii) from said regular CPMG measurements into combined T.sub.2 spectrum data; and

extracting information about attributes of said earth formation from said combined T.sub.2 spectrum data, wherein the difference in the depth of investigation in (i) and (ii) is used to estimate the true movable fluid contents of the earth formation.

15. The method of claim 1 further comprising the steps of obtaining time domain data corresponding to response signals from said one or more regular NMR pulse trains; combining time domain data obtained from (i) said stacked short NMR pulse trains and (ii) from said regular CPMG trains; and

extracting information about attributes of said earth formation from said combined data.

16. An NMR borehole logging method for measuring an indication of petrophysical attributes of an earth formation, the method comprising the steps of:

(a) applying in a pre-determined sequence at least two short NMR pulse trains, each pulse train comprising at least one pulse and resulting in at least one response signal from said earth formation, the interval T.sub.s between any two short pulse trains being less than the time required for polarization of substantially all nuclear magnetization in any bulk fluid contained in said earth formation; and

(b) stacking NMR response signals from said at least two short NMR pulse trains to obtain time domain data indicative of fast decay components of a fluid state contained in said earth formation;

(c) combining said at least two short NMR pulse trains with regular Carr-Purcell-Meiboom-Gill (CPMG) pulse-echo measurements of said earth formation, wherein a regular CPMG pulse-echo train is preceded by a recovery time T.sub.w

sufficient to substantially polarize all nuclear magnetization in the fluid state; and

(d) determining overall relaxation properties of the fluid state contained in said earth formation from the combination of said least two short NMR pulse trains with said regular CPMG pulse-echo measurements.

18. The method of claim 17 wherein said at least two short NMR pulse trains are Carr-Purcell-Meiboom-Gill (CPMG) pulse-echo trains.

20. The method of claim 17 further comprising the step of identifying a portion of the T_{sub.2} spectrum as corresponding to very heavy crude hydrocarbons, such as bitumen.

21. The method of claim 17 further comprising the step of identifying a portion of the T_{sub.2} spectrum as corresponding to clay-bound fluids.

22. The method of claim 17 wherein an indication of petrophysical attributes of the earth formation is provided by interpreting external resistivity measurements data in view of the portion of the T_{sub.2} spectrum identified as corresponding to clay-bound fluids.

23. The method of claim 16 further comprising the steps of converting the time domain data into T_{sub.2} spectrum data; and

determining attributes of said earth formation from the T_{sub.2} spectrum data.

24. The method of claim 23 wherein an indication of petrophysical attributes of the earth formation is provided by associating increasing cation exchange capacitance (CEC) values to porosity components with decreasing T_{sub.2} relaxation values in the T₂ spectrum.

25. The method of claim 16 further comprising the step of converting time domain data obtained from (i) said stacked short NMR pulse trains and (ii) from said regular pulse-echo measurements into combined T_{sub.2} spectrum data; and

extracting information about attributes of said earth formation from said combined T_{sub.2} spectrum data.

26. The method of claim 25 wherein the petrophysical attributes of the earth formation comprises the clay minerals content which is determined on the basis of components of the T_{sub.2} spectrum.

27. The method of claim 25 wherein said attributes of said earth formation comprises the total magnetic resonance porosity .PHI.._{sub}.MRT of said materials which is computed as:

$$.PHI.._{sub}.MRT = .PHI.._{sub}.MRE + .PHI.._{sub}.CIB$$

where:

.PHI.._{sub}.MRE is the magnetic resonance effective porosity derived from components in the combined T_{sub.2} spectrum that correspond to said regular pulse-echo measurements, and

.PHI.._{sub}.CIB is the bound porosity derived from components in the combined T_{sub.2} spectrum that correspond to said stacked short NMR pulse trains.

29. The method of claim 27 further comprising the step of combining the magnetic resonance total porosity .PHI.._{sub}.MRT with an external measure of the total porosity .PHI.._{sub}.T to derive additional information about petrophysical attributes of the earth formation, such additional information comprising an estimate of the saturations of oil and gas in the earth formation.

31. The method of claim 16 wherein said short NMR pulse trains and said regular CPMG trains are applied in a single pass through the borehole.

32. The method of claim 16 wherein said short NMR pulse trains and said regular CPMG trains are applied in separate passes through the borehole.

33. The method of claim 16 further comprising the step of identifying a portion of the fast T.sub.2 spectrum as fluids bound to clays susceptible to swelling, such as smectites and illites.

34. The method of claim 16 further comprising the step of combining short CPMG trains with CPMG trains with reduced recovery time sufficient to polarize substantially all nuclear magnetization from fluids in a bound state and insufficient to polarize all nuclear magnetization from fluids in an unbound fluid state of the earth formation.

35. The method of claim 34 wherein said short CPMG trains and said CPMG trains with reduced recovery time are applied in a single pass through the borehole.

36. The method of claim 34 wherein said short CPMG trains and said CPMG trains with reduced recovery time are applied in separate passes through the borehole.

37. The method of claim 34 wherein the petrophysical attributes of the earth formation comprises the total bound fluid porosity .PHI..sub.BT of the earth formation computed as:

$$.PHI..sub.BT = .PHI..sub.CIB + .PHI..sub.CapB$$

where .PHI..sub.CIB is the clay bound porosity determined from said short CPMG trains, and .PHI..sub.CapB is the capillary bound porosity determined from said CPMG trains with reduced recovery time.

46. An NMR method for measuring an indication of an attribute of a volume of earth formation in a borehole, comprising the steps of:

a) applying oscillating magnetic fields according to a pre-specified pulse sequence, said pulse sequence comprising: a regular Carr-Purcell-Meiboom-Gill (CPMG) train having between about 100 and 10,000 echoes, followed by at least one short wait interval T.sub.s of approximately 10-100 ms duration, followed next by at least one short CPMG train having between about 1 and 100 echoes;

b) measuring NMR signals representing spin-echo relaxation of a population of particles in the geologic structure; and

c) processing NMR signals corresponding to said regular CPMG train and NMR signals corresponding to said at least one short CPMG train to determine values for the magnetic resonance effective porosity (.PHI..sub.MRE) of the volume of the earth formation and values for the clay-bound porosity .PHI..sub.CIB of the volume of the earth formation.

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☐ 1. Document ID: US 20020167314 A1

L37: Entry 1 of 7

File: PGPB

Nov 14, 2002

PGPUB-DOCUMENT-NUMBER: 20020167314

PGPUB-FILING-TYPE: new

DOCUMENT-IDENTIFIER: US 20020167314 A1

TITLE: System and method for determining oil, water and gas saturations for low-field gradient NMR logging tools

PUBLICATION-DATE: November 14, 2002

INVENTOR-INFORMATION:

| NAME | CITY | STATE | COUNTRY | RULE-47 |
|------------------|------------|-------|---------|---------|
| Prammer, Manfred | Downington | PA | US | |

US-CL-CURRENT: 324/303

| | | | | | | | | | | |
|------------|-------|----------|-------|--------|----------------|------|-----------|-----------|-------------|------|
| Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC |
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☐ 2. Document ID: US 6525534 B2

L37: Entry 2 of 7

File: USPT

Feb 25, 2003

US-PAT-NO: 6525534

DOCUMENT-IDENTIFIER: US 6525534 B2

TITLE: System and methods for NMR signal processing without phase alternated pair stacking

DATE-ISSUED: February 25, 2003

INVENTOR-INFORMATION:

| NAME | CITY | STATE | ZIP CODE | COUNTRY |
|-------------------|----------|-------|----------|---------|
| Akkurt; Ridvan | Kingwood | TX | | |
| Cherry; Ronald E. | Kingwood | TX | | |

US-CL-CURRENT: 324/303; 324/300

| | | | | | | | | | | |
|------------|-------|----------|-------|--------|----------------|------|-----------|-----------|-------------|------|
| Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC |
| Drawn Desc | Image | | | | | | | | | |

☐ 3. Document ID: US 6512371 B2

L37: Entry 3 of 7

File: USPT

Jan 28, 2003

US-PAT-NO: 6512371
DOCUMENT-IDENTIFIER: US 6512371 B2

TITLE: System and method for determining oil, water and gas saturations for low-field gradient NMR logging tools

DATE-ISSUED: January 28, 2003

INVENTOR-INFORMATION:

| NAME | CITY | STATE | ZIP CODE | COUNTRY |
|------------------|------------|-------|----------|---------|
| Prammer; Manfred | Downington | PA | | |

US-CL-CURRENT: 324/303

| Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC |
|------------|-------|----------|-------|--------|----------------|------|-----------|-----------|-------------|------|
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☐ 4. Document ID: US 6400147 B1

L37: Entry 4 of 7

File: USPT

Jun 4, 2002

US-PAT-NO: 6400147
DOCUMENT-IDENTIFIER: US 6400147 B1

TITLE: Downhole NMR tool having a programmable pulse sequencer

DATE-ISSUED: June 4, 2002

INVENTOR-INFORMATION:

| NAME | CITY | STATE | ZIP CODE | COUNTRY |
|-----------------------|----------|-------|----------|---------|
| Toufaily; Ali K. | Richmond | TX | | |
| Sezginer; Abdurrahman | Houston | TX | | |
| Jorion; Bruno | Houston | TX | | |
| Depavia; Luis E. | Houston | TX | | |

US-CL-CURRENT: 324/303; 324/300

| Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | KWIC |
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☐ 5. Document ID: US 6297632 B1

L37: Entry 5 of 7

File: USPT

Oct 2, 2001

US-PAT-NO: 6297632
DOCUMENT-IDENTIFIER: US 6297632 B1

TITLE: Detecting tool motion effects on spin echoes obtained with nuclear magnetic resonance measurements

DATE-ISSUED: October 2, 2001

INVENTOR-INFORMATION:

| NAME | CITY | STATE | ZIP CODE | COUNTRY |
|---------------|----------|-------|----------|---------|
| Speier; Peter | Stafford | TX | | |

US-CL-CURRENT: 324/303

| Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments |
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☐ 6. Document ID: US 6242912 B1

L37: Entry 6 of 7

File: USPT

Jun 5, 2001

US-PAT-NO: 6242912

DOCUMENT-IDENTIFIER: US 6242912 B1

TITLE: System and method for lithology-independent gas detection using multifrequency gradient NMR logging

DATE-ISSUED: June 5, 2001

INVENTOR-INFORMATION:

| NAME | CITY | STATE | ZIP CODE | COUNTRY |
|---------------------|--------------|-------|----------|---------|
| Prammer; Manfred G. | West Chester | PA | | |
| Mardon; Duncan | Kingwood | TX | | |
| Coates; George R. | Austin | TX | | |
| Miller; Melvin N. | Wynnewood | PA | | |

US-CL-CURRENT: 324/303; 324/307

| Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments |
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☐ 7. Document ID: WO 9714063 A1 AU 9671172 A NO 9801328 A EP 852737 A1 US 5936405 A AU 716950 B US 6242912 B1

L37: Entry 7 of 7

File: DWPI

Apr 17, 1997

DERWENT-ACC-NO: 1997-236054

DERWENT-WEEK: 199721

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TITLE: Lithology-independent gradient NMR gas detection - for detecting the presence and estimating the quantity of gaseous and liquid hydrocarbons in a near wellbore zone

| Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments |
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